# AIR SEALING AS A MEANS OF ABATING ACID MINE DRAINAGE POLLUTION

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## ABSTRACT

The oxidation of iron sulfides in a coal mine in the presence of excess moisture results in the formation of free sulfuric acid. The acid may be transported by the mine discharge to streams where it constitutes a major pollutant in several Appalachian States.

Both field and laboratory tests indicate that if oxygen can be excluded from an abandoned coal mine, the oxidation of pyrite will be prevented and acidity of the mine discharge reduced.

The Bureau of Mines has selected a small abandoned mine with a highly acid discharge and plans to seal it to prevent air from entering it. A study of the geologic and hydrologic environment of the mine is expected to serve as a basis for comparing the quality of the mine discharge before and after sealing and to aid in evaluating the effectiveness of mine air sealing.

Certain relationships of dissolved solids and total acidity to the flow rate were determined and explained as dilution or climatological effects. These relationships must be considered in any evaluation of changes in the quality of the mine discharge.

## INTRODUCTION

When coal deposits are exposed to natural weathering and erosion, the iron sulfides contained in the coal and adjacent strata oxidize to form new compounds consisting of ferrous sulfate and free sulfuric acid. Oxygen in the atmosphere further oxidizes the ferrous sulfate to ferric sulfate, which then hydrolyzes in an excess of water to insoluble iron hydrates known as "yellow boy," and sulfuric acid. The coal itself is largely unreactive and subject only to mechanical disintegration. Figure 1 summarizes the essential reactions believed to take place during the oxidation of iron sulfides.

Removal of the coalbed by mining exposes large surface areas to oxidation and greatly accelerates an otherwise slow natural process. Mining also may drain ground water from the surrounding strata and this seepage will dissolve the acid salts formed in the mine and transport them to the streams.

So-called sulfur water was recognized several hundred years ago as being common to the coal mining districts in England and first was observed in the United States about 1698, long before commercial mining began. In 1803, a reference was made to sulfurous water issuing from coal outcrop near Pittsburgh, Pa.; by 1890, acid drainage from coal mines in western Pennsylvania was blamed for extensive fish kills in the Youghiogheny River at McKeesport.

A combination of four factors--extensive coal mining, abundant rainfall which produces large quantities of mine water and runoff, a low natural alkalinity of the streams, and the presence of pyrite in the coal--are responsible for the concentration of acid mine drainage problems in the Eastern Mountain States from Pennsylvania to Alabama. Acid drainage from mine sites usually reaches the major rivers via small tributaries.

In a recent special report prepared for the House of Representatives Committee on Government Operations, Subcommittee on Natural Resources and Power, it is claimed that the effects of acid mine drainage pollution are felt by more than 10 million people living in metropolitan and industrial areas of the East.

The problem in the Appalachian Region has become progressively worse in this century because of the large increase in the number of abandoned mines, and because water pollution does not necessarily end when mining is discontinued. The chief offenders are the abandoned above drainage mines from which water may continue to flow indefinitely. However, all such mines do not produce acid water. In many instances the hydrologic and geologic environment is the controlling factor.

In 1924, the U.S. Public Health Service made a study of stream pollution which included an investigation of the possibility of air sealing abandoned deep mines above drainage so as to prevent oxidation and the formation of sulfuric acid.

The basis for mine sealing lies in these two nearly incontestable facts:

1. Exclusion of air from sulfide material prevents its oxidation.[1]

2. Reducing the amount of water passing through a mine reduces the acid load put into the streams receiving the effluent.[2]

In 1933, the Bureau of Mines issued a report which recommended the air sealing of abandoned mines in ten Eastern States. Consequently, between 1935 and 1938, and again from 1947 to 1950, hundreds of masonry seals were placed in abandoned drift mines by State and Federal organizations. Dry drifts were closed with a simple masonry block air seal, but mine openings through which water was flowing were equipped with a trap which allowed the water to flow out but prevented air from entering.

The sealings were not followed up with a detailed study of the change in water quality; however, general observations showed the results to be favorable, with a substantial initial reduction in the quantity of acid in streams receiving the mine drainage. Some of the seals since have deteriorated, some sealed mines have been reopened, and numerous additional abandoned mines are not presently sealed.

Preliminary results of recent laboratory investigations conducted by the Bureau of Mines seem to offer a positive technical reason for pursuing mine sealing as a means for abatement of acid pollution. Using the Warburg manometric apparatus to determine the effect of oxygen deficiency on the reactivity of pyrite in the presence of water, the atmosphere was varied in the sealed vessel from normal air to 100 per cent nitrogen. After each test, which ranged from 1 to 4 days, the total iron in solution was determined as a measure of the oxidation of pyrite.

After the first day, the amount of iron in solution was directly proportional to the oxygen content of the atmosphere and to the exposure time. With the nitrogen atmosphere, the iron in solution remained constant at a negligible value throughout the test period.

Technical reports on acid mine drainage range over many aspects of the problem but few deal with actual case histories of individual mine sealing and the effectiveness of mine air sealing as a means of abating acid mine water pollution. Clearly, what is needed is more data on sealing and the natural environment of the mine.

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1/ Braley, S. A. Acid Mine-Drainage VI. Control of Oxidation. Mechanization, v. 18, No. 6, 1954, pp. 105-107.

2/ Pennsylvania, Commonwealth of. Control of Acid Drainage From Coal Mines. Dept. of Health, Sanitary Water Board, 1952, 28 pp.

Early in 1962, the Bureau of Mines and the Coal Industry Advisory Committee to the Ohio River Valley Water Sanitation Commission (ORSANCO) entered into a cooperative agreement to conduct research in acid mine drainage. One of the projects is to evaluate mine sealing as a means of reducing the discharge of acid mine water from abandoned deep coal mines above drainage. As prerequisites to the field study, it was necessary to locate a small abandoned underground mine having a minimum number of openings, isolated from any active workings, and currently discharging acid water. An investigation of possible sites was made and a mine near Kittanning, Armstrong County, Pa., was selected. Cooperative agreements also were signed by the Bureau of Mines, the property owner, and the former operator of the mine, who supplied a map of the underground workings.

This mine affords a good example of the stream pollution which can result from the acid drainage from only one small mine. The total acid load, which is volume times acidity of the mine discharge for 182 days, sampled at random throughout the year of 1964, was equal to 41 tons of sulfuric acid. Therefore, the estimated acid load for the entire year would equal approximately 80 tons, which flows directly into a major tributary of the Allegheny River.

A prefabricated building was erected at the mouth of the mine drainage drift in May 1963 to house equipment for the continuous monitoring of the pH, conductivity, Eh, and flow rate of the mine effluent. An automatic sampler was installed, and all mine water was diverted through a V-notch weir. A continuous record of the quality and quantity of the water has been maintained since September 1963.

In the summer of 1964, a study of the geologic and hydrologic conditions of the mine was initiated so that a better understanding and interpretation of the results of mine sealing might be achieved. In December 1964, a topographic base map of the mine property was prepared from aerial photographs and later a map of the mine workings was superimposed on the topographic map.

In December 1964, four diamond drill holes and two shallow auger holes were drilled to gather additional information on geologic strata, ground water, and mine subsidence. The drill holes also are used, where possible, to collect samples of the mine atmosphere.

The Bureau of Mines plans to air seal the mine this year. The four dry mine openings are to be closed with masonry blocks and mortar, then coated on the outside with urethane foam to assure an airtight seal. The drainage drift seal also is to be of a masonry type structure, provided with a trap, which permits the outflow of water but prevents the inflow of air. Copper tubes are to be placed in all five seals so that samples of mine atmosphere can be collected periodically to test for oxygen depletion. Air samples collected prior to sealing show a normal oxygen content.

## GENERAL GEOLOGY

The mine is located in the Allegheny Plateau, a region of virtually horizontal sedimentary strata which have been eroded by streams to form a dissected, hilly topography. The poorly exposed bedrock belongs to the lower part of the Conemaugh series and the upper part of the Allegheny series, both of the Pennsylvanian system. The beds are composed predominately of siltstone and sandstone with minor amounts of claystone, limestone, and coal.

The mine was worked in the Upper Freeport coalbed, which is the top formation in the Allegheny series. It is the only coal of economic importance in the immediate area. It is a bright banded, moderately low sulfur coal, 42 inches thick. The coal seam lies above drainage and was mined from beneath a "peninsula" in the topography. It outcrops on three sides of the hill but to the northeast is under higher topography and deeper cover, which ranges up to 200 feet thick. Structure contours on the base of the coal seam show a dip of about 1 degree to the south, although at the south end of the property the beds which are exposed in a highwall dip slightly to the north. Mine drainage, therefore, is generally to the southeast.

Surface water is absent from the mine property except during heavy thaw or precipitation. Surface drainage from the hill overlying the mine is by means of small perennial streams in the valley on each side of the hill, which are tributaries to Cowanshannock Creek. The mine effluent of pH 3.1 flows into one of these tributaries The pH of Cowanshannock Creek above this tributary is 7.2 and below is 6.2. The cree is more than 20 times as great in volume of flow at low level than the stream carrying the mine discharge.

## CLIMATE

The climate of the Kittanning area has a direct bearing on the ground water con ditions at the mine. Precipitation is distributed fairly evenly throughout the year June, July, and August are months of maximum evapotranspiration and lowest mine drainage rate, while highest surface runoff and maximum ground water recharge occur during the January to April period when mine drainage rates are highest.

About 46 percent of the land immediately overlying the mine workings is covered by stands of mixed hardwoods which fringe the hill. The remainder of the land is covered by an open grassland growing on the gently sloping hilltop. Figure 2 gives a general view of the setting.

## HISTORY OF MINING

Some time prior to 1929, coal was dug from two small drifts on the property; in 1942, one of these drifts was reopened and briefly used as the entry for a small mi

In 1952, coal was stripped from along the southwest and southeast sides of the hill. The stripping was backfilled but not restored to contour. From later in 195 until 1958, the coal was deep mined by conventional methods with good roof conditio and relatively little water seepage. Beginning in 1958, the remaining pillars of coal were mined; by 1959, all recoverable coal had been removed. The main entries were sealed in 1962 for safety purposes. The former operators reported a moderate increase in mine water after the pillars were mined.

During and after mining, there was surface subsidence within a small area alon the northern limit of the property, but no other evidence of surface subsidence was observed.

## SULFUR BURDEN OF ROCKS

It has been well established in the literature that the source of sulfur essen tial for the formation of acid mine water is in the iron sulfides, which are erratically distributed throughout the coal and adjacent rocks. Organic sulfur compound associated with coal are not sufficiently reactive to contribute to the formation c acid mine water.

Channel samples of the coal from the mine have an average pyritic sulfur conte of 0.35 percent. Low values of 0.17 to 0.36 percent also were determined from sam ples of roof rock, while gob recovered from the old workings contained an average c 2.00 percent pyritic sulfur. The highest and, also, most erratic values were found in the layer of underclay, just below the coal. These ranged from 0.27 to 17.28 p cent. It, therefore, appears that most of the sulfur in the mine occurs in the go piles and the top layer of underclay.

## DIAMOND DRILLING

In order to gather as much information as possible on the environment of the mine, four core holes were drilled into the strata overlying the mine workings and two auger holes were drilled in the spoil banks or backfill from the strip mining.

In brief, the core holes showed the following:

1. Depth to bedrock was 10 to 12 feet.

2. Bedrock was soft or oxidized to a maximum depth of 95 feet.

3. Fracturing due to mine subsidence was not evident.

4. Core recovery was good.

5. Siltstone was the most abundant rock type.

6. Laboratory tests on water permeability of the sandstone showed only 0.01 md.

7. The mine workings were largely filled by caving or heaving of the floor, although conditions varied.

8. Only one of the four holes retained any water above the mine workings.

9. Limestone occurs only below the coal seam and underclay and can have little neutralizing effect on the mine water.

## GROUND WATER

The flow rate of the mine discharge ranges from 6 to 632 gpm and is dependent chiefly on the season and quantity of precipitation. The base flow of 6 to 8 gpm persists throughout prolonged dry spells and is derived from ground water storage depletion, while peak flows are associated with late winter and spring precipitation and thaws. The graph shown in figure 3 covers only a 1-year period but is representative of these relationships. The graph also shows that the acid load of the mine effluent, which is a product of acidity times flow rate, is proportional to the flow rate. Similar proportions and seasonal effects on mine flow rates have been reported by S. A. Braley.[3]

The graph shows a lag in response of the flow rate to precipitation of from 3 to 5 days, indicative of the time required for water to percolate from the surface to the mine workings.

In calendar year 1964, which was selected for analysis, a total of 41.96 inches of precipitation was recorded. During the same period, total mine effluent was equivalent to 12.84 inches of precipitation for a 92-1/2-acre area. These values suggest that about 30 percent of the precipitation over the area infiltrates downward into the mine; the remaining 70 percent is retained as aquifer recharge or is lost as runoff and evapotranspiration. This is in general agreement with the work of Carpenter and Davidson,[4] who found that the quantity of drainage from shallow mines in western Pennsylvania equaled about 25 percent of the precipitation above the mine.

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3/ Braley, S. A. Acid Mine Drainage IV. Composition and Flow. Mechanization, v. 18, No. 4, 1954, pp. 137-138.

4/ Carpenter, L. V. and A. H. Davidson. Development in the Treatment of Acid Mine Drainage. West Virginia Univ. Assoc. Bull. 2, No. 4, 1930, pp. 50 to 57.

The high rate of infiltration occurs chiefly during the dormant season and appears to be facilitated by the gentle slope of the topography, a natural permeability of the soil, and subsidence fractures in the bedrock.

The presence of subsidence fractures may be inferred from the fact that pillars were removed from much of the mine and from the loss of three springs on the property during the course of mining. The relative soil infiltration rate was determined by using the double ring infiltrometer on different soil types above the mine and, for purposes of comparison, on materials of similar or contrasting properties from other localities. Results show that the soil types above the mine may be classified as highly permeable and capable of transmitting relatively large amounts of meteoric water to the subsoil and bedrock.

## GEOCHEMISTRY OF GROUND WATER

Drainage from the mine consists of ground water which has derived its chemical composition chiefly while percolating downward through the overburden and passing through the mine workings. It is characterized by high acidity and a high concentration of dissolved solids. The temperature of the water from the mine virtually is constant at $52^{\circ}$ F.

Other nearly constant qualities of the mine water are the pH and Eh, which fluctuate within the narrow range of 3.0 to 3.2 and 625 to 825 mv, respectively. Conductivity varies over a moderate range of 1,400 to 2,600 micromho. It correlates closely with the fluctuation in dissolved solids content of which iron sulfate constitutes the major percentage. Total acidity, measured in terms of equivalent $CaCO_3$, ranged from 180 to 950 ppm and showed a correlation with the total iron content of the mine water since sulfates other than iron contribute very little to the total acidity; the dissolved solids concentration is an approximate index of the total acidity under the current conditions. Figure 4 shows the results of plotting the mine effluent flow rate against 139 total dissolved solids analyses which are separated, according to the time of sampling, into growing and dormant season for the period of October 1963 to October 1964. Two features of the plot are particularly outstanding: The contrast in solute between the dormant and growing season, and the correlation of dormant season solute and flow rate below 300 gpm. High flow rates were not determined. The solute concentration is inversely proportional to the flow rates below 300 gpm reflecting the dilution effect of increased flow. At discharges greater than 300 gpm, the above effect apparently is overcome by a flushing action in the mine whereby higher water levels dissolve an accumulation of highly acid salts which have formed as a result of the oxidation of iron sulfides. In flow rates of less than 150 gpm, there is more solute in the mine water during the dormant season than the growing season. As yet, there is no satisfactory explanation for this relationship. Similar relationships were observed between total acidity and flow rate.

## DISCUSSION

We have attempted to determine the environmental conditions of the mine and have collected data on the volume and quality of the mine discharge so that we have a basis for comparing water quality before and after sealing and, therefore, can evaluate the effectiveness of air sealing in reducing the acidity. We have tried to determine the source of the mine water in order to try to divert or seal off surface water and reduce the acid load of the effluent. The high infiltration rate and permeability of the overburden to water suggest that we may not be successful in this direction.

$$\overset{\text{Iron sulfide (pyrite)}}{2FeS_2} + \overset{\text{Atmospheric oxygen}}{7O_2} + \overset{\text{Water}}{2H_2O} \longrightarrow \overset{\text{Ferrous sulfate}}{2FeSO_4} + \overset{\text{Sulfuric acid}}{2H_2SO_4}$$

OXIDATION OF IRON SULFIDE

$$\overset{\text{Ferrous sulfate}}{4FeSO_4} + \overset{\text{Sulfuric acid}}{2H_2SO_4} + \overset{\text{Atmospheric oxygen}}{O_2} \longrightarrow \overset{\text{Ferric sulfate}}{2Fe_2(SO_4)_3} + \overset{\text{Water}}{2H_2O}$$

OXIDATION OF FERROUS SULFATE

$$\overset{\text{Ferric sulfate}}{Fe_2(SO_4)_3} + \overset{\text{Water}}{6H_2O} \longrightarrow \overset{\text{Ferric hydrate}}{2Fe(OH)_3} + \overset{\text{Sulfuric acid}}{3H_2SO_4}$$

HYDROLYSIS OF FERRIC SULFATE

FIGURE 1. - Summary of the Reactions Involved in the Formation of Acid Mine Water

FIGURE 2. - General View of the Mine Property

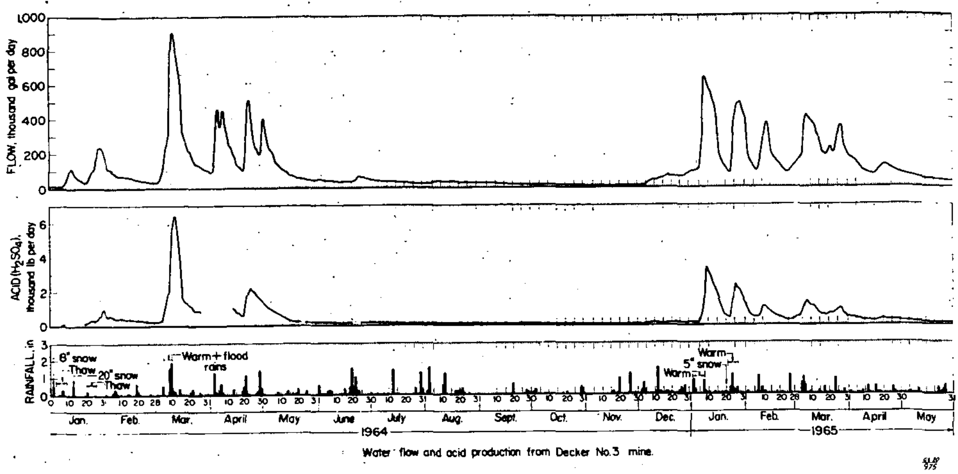


FIGURE 3. - Graph Showing the Relationship of Mine Effluent Flow Rate to Precipitation

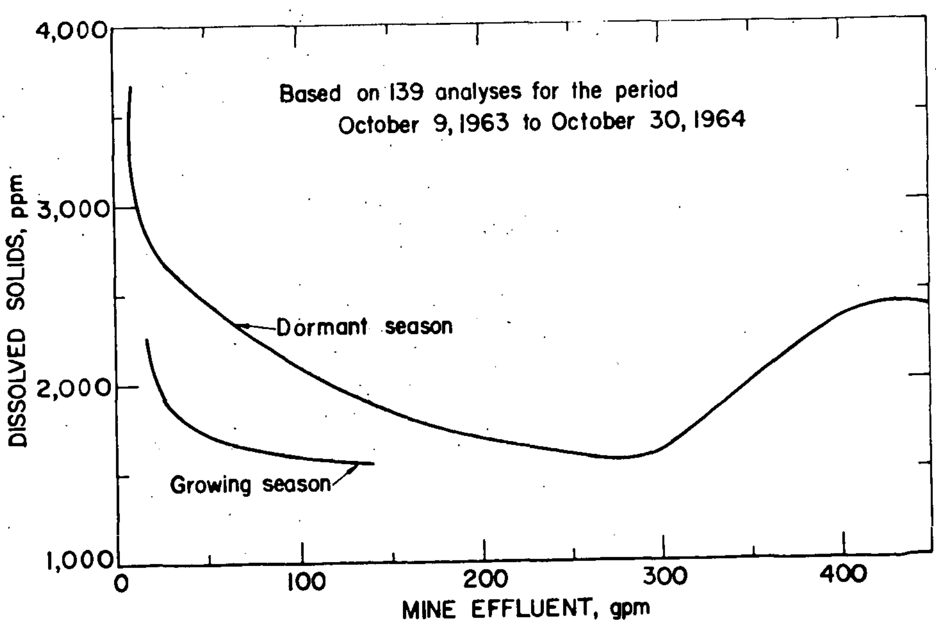


FIGURE 4. - Graph Showing the Relationship of Total Dissolved Solids Concentration to the Mine Effluent Flow Rate